

ISSN 1848-0071
543.612.3+66.098.4=111
Received: 2017-09-12
Accepted: 2018-01-22
Professional paper

OPTIMIZING PROCESS CONTROL OF THE ANAEROBIC DIGESTION OF ORGANIC MATTER

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The paper was presented at 4 th International Symposium on Environmental Management -
Towards Circular Economy, December 7th – 9 th 2016, Zagreb, Croatia

The proper process control is the key to achieving both environmental and commercial goals of conducting the process of anaerobic digestion. Taking into account that the parameters that can be monitored are quite numerous, and that the monitoring equipment, its installation and maintenance require significant financial resources, it is, from commercial aspect, necessary to minimize the number of parameters to the set of parameters which are necessary but sufficient for the proper conduct of the process to the point after which the further continuation of the process is not economically justified. The paper presents the model developed for determination of the minimum number of parameters to be monitored in order to ensure sufficient quality control of this process and describes its validation through the laboratory test.

Key words: anaerobic digestion, organic waste, biogas, process control parameters.

Optimizacija vođenja procesa anaerobne razgradnje organskog otpada. Pravilno vođenje procesa je ključ za postizanje ekoloških i ekonomskih ciljeva u provedbi procesa anaerobne razgradnje. Uzimajući u obzir brojne parametre provedbe procesa koji se mogu pratiti i to da instalacija, održavanje i nadgledanje opreme zahtjevaju značajna finansijska sredstva, potrebno je, s ekonomskog aspekta, minimalizirati skup parametara do razine koja će biti dovoljna za pravilno vođenje procesa do trenutka nakon kojeg daljnji nastavak procesa nije ekonomski opravdan. U radu je predstavljen razvijeni model za određivanje minimalnog broja parametara koji se prate kako bi se osigurala dovoljna kontrola kvalitete procesa i opisana je validacija modela kroz laboratorijski test.

Ključne riječi: anaerobna digestija, organski otpad, bioplin, parametric vođenja procesa.

INTRODUCTION

Anaerobic digestion of organic matter with biogas as a main product became economically cost-effective variant for processing the large quantities of organic waste. The importance of this technology is reflected either in the economic and environmental benefits [1, 2]. The anaerobic treatment of waste in the world is recognized as a process that significantly affects the reduction of greenhouse gases, which largely

reflected the environmental impact [3, 4, 5]. In recent decades the process of anaerobic digestion has become widespread in many countries in Europe, thanks to legislation which aims to increase the production of biogas in different sectors [6]. Anaerobic treatment of waste reduces foul odor, human and animal infections, as well as pollution of water, air and soil [7]. In a biogas plant, the results of the process of anaerobic digestion

are biogas and digestate. Biogas is a combustible gas, consisting primarily of methane and carbon dioxide, and is used directly for the production of heat and/or electricity, as an alternative to fossil fuels. Digestate is the substrate, produced in anaerobic processes, and can be used as fertilizer, thereby reducing the need for mineral fertilizers. In addition, digestate contains nitrogen in the form of minerals (ammonia) which is useful for plants, because it is extremely easy to enrich the arable land, and the plants take it easier than organic nitrogen. The production of biogas through anaerobic digestion offers significant advantages over other forms of waste treatment [8, 9, 10].

It should be noted that the anaerobic digestion takes place only under specific conditions, and the efficiency of the anaerobic process depends on several key parameters, therefore it is very important to ensure optimal conditions for the development of anaerobic microorganisms. The growth and activity are under the strong

influence of temperature, pH, nutrient availability, mixing intensity, presence of inhibitors, and the lack of oxygen, because methane bacteria are strict anaerobes so the any presence of oxygen in the digester has to be prevented. In the current process of anaerobic digestion, in addition to the above parameters, the type and composition of the substrate also have great affect, as well as the hydraulic retention time of the substrate in the reactor and the rate of input of organic matter in the reactor. However, different materials require different conditions as well as the time of the retention of the organic matter in the digester in order to ensure its complete degradation. Terms used for the blending tank are obviously different, but always talking about the same thing, regardless whether the words “digester, fermenter, bioreactor, anaerobic reactor” or another one is used, it is always a closed container in which the microbiological and chemical decomposition reactions of organic matter without oxygen are taking place [9, 11].

DETERMINATION OF PARAMETERS FOR CONTROL

Whatever the substrate is, the control of anaerobic processes can be carried out by measuring the number of physical and chemical parameters in the reactor. This series includes monitoring of pH, conductivity, total dry matter content, organic matter content, the content of suspended matter, the content of suspended organic matter, chemical oxygen demand, biological oxygen demand, total carbon content, the content of total nitrogen, content of Kjeldahl nitrogen, phosphorus content, the potassium content, temperature, pressure, concentration of ammonia, the concentration of volatile fatty acids, protein content, fat content, alkalinity, concentration of certain heavy metals, and other toxic substances.

The above mentioned parameters are directly related to the characteristics of the substrate, while there is a lot of parameters other than those specified here, which are monitored in some specific situations. In addition, it is very important to determine the quantity and composition of the produced biogas, and provide anaerobic conditions in the reactor.

When it comes to the application of anaerobic digestion in industrial proportion, for obtaining biogas, very important parameters which influence the course of the process and the quality and yield of the final products are, in addition to the above-mentioned characteristics of the substrate, the retention time of the substrate and amount of organic matter introduced into the

digester. These parameters are important for the continuous anaerobic processes, while in discontinuous ones they do not affect the running of the process, depending on the type and mode of operation of the reactor.

In everyday practice, not all the parameters listed are monitored, but only those that are absolutely necessary to follow in order to drive the process successfully,

and consequently, to achieve the desired result, but avoiding excessive unnecessary costs. In order to determine the minimal but sufficient set of parameters for control, various paths are possible and one of them is proposed here (see Figure 1). In order to check the validity of that method, a laboratory test was performed and described below.

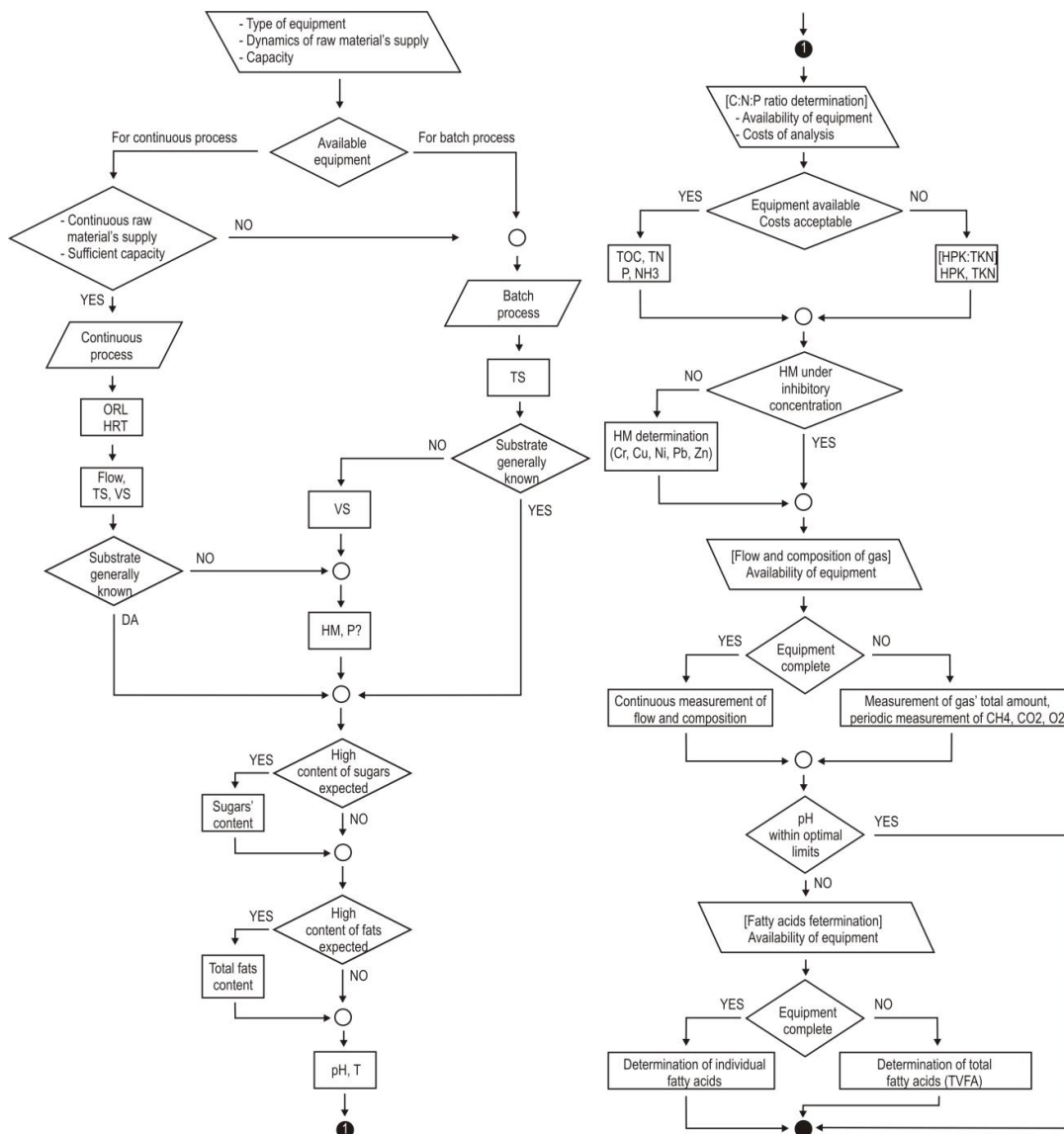


Figure 1. Algorithm for determining a set of parameters for control the process of anaerobic digestion of organic matter

Slika 1. Algoritam za određivanje seta parametara pri vođenju procesa anaerobne razgradnje organske tvari

MATERIALS AND METHODS

For the purposes of this paper, a laboratory reactor system for anaerobic digestion of organic matter with glass eudiometric pipes (manufacturer's Šurlan-Medulin), mounted on glass bottles (usable volume of 500 mL) has been used. Provision of anaerobic conditions was performed by sparging of nitrogen in order to displace the air from the reactor, while providing the required constant temperature of the reactor system at $35\text{ °C} \pm 2\text{ °C}$ has been carried out by heating in a water bath with circulating

water (Figure 1). Using the eudiometric pipes, the production of biogas is simple to read off, because produced gas pushes the liquid level down, while the fluid goes back into the storage bottle.

The pressure and temperature of the ambient air were measured on the set pressure hydrometers or eudiometric tubes, whose values are used to convert the volume of the resulting biogas to normal conditions. Mixing of the substrate is realized mechanically using a magnetic stirrer.

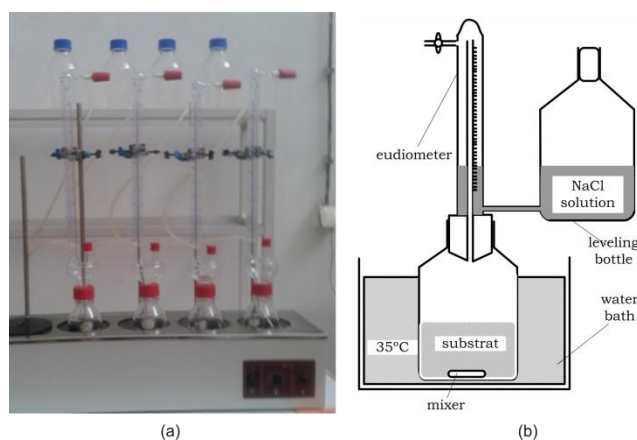


Figure 2. Laboratory reactor system: (a) system layout; (b) reactor block scheme

Slika 2. Laboratorijska izvedba reaktorskog sustava: (a) izgled sustava; (b) shema reaktora

As the base substrate, sewage sludge from treatment plants of urban waste water (located in Srebrenik) has been used. To test the effects of additives to sewage sludge the next co-digestats were used, which were added in different proportions:

- Animal excrement - waste left behind after the rest of the breeding of broiler chickens from the company "Pilkom" Gradačac Ltd.;
- Organic fraction of municipal solid waste - food scraps from Students' restaurants, University of Tuzla;

- Waste from the food industry - the rest after the processing of fruit and vegetables from the company "Fana" Ltd. Srebrenik.

The temperature has been determined by direct measurement, using a mercury thermometer. Determination of dry and volatile organic matter has been performed according to Method 2540-B and 2540 Solid-Solid E [12]. Electrometric measurement of pH was carried out by direct measurement, with the pH meter METTLER TOLEDO FE 20/EL 20. Prior to each measurement, internal control was

performed with certified reference materials of pH-value 4.1; 7.01; 10.01. The nitrogen content by Kjeldahl has been determined according to Method 4500-N_{org} B [12]. The method consists of three stages: digestion at a temperature of 340 °C (boiling point of H₂SO₄) in the presence of concentrated sulfuric acid and selenium Kjeldahl catalyst; distillation in the presence of NaOH where distillate accepts in the solution of boric acid, and titration with 0.1 M HCl in the presence of indicator bromocresol green. Determination has been made on Kjeldahl apparatus Gerhardt. The concentration of ammonia nitrogen has been determined according to Method 4500-NH₃ C [12]. With the known values of ammonia nitrogen, pH-values and temperature prevailing in the reactor, the concentration of free ammonia is calculated according to the equation obtained from chemical equilibrium:

$$[\text{NH}_3] = \frac{[\text{NH}_3 + \text{NH}_4]}{1 + \frac{\text{H}^+}{K_a}}$$

The volatile fatty acids are formed as an intermediate in the production of biogas, and the concentration of volatile fatty acids

RESULTS AND DISCUSSION

Temperature stability is crucial to the running of the anaerobic process. The duration of the anaerobic digestion process is directly related to the temperature at which it takes place. It is possible to distinguish three temperature zones: psychrophilic (below 25 °C), mesophilic (25-45 °C) and thermophilic (45-70 °C) [17, 18, 19, 20, 21]. The temperature can be measured in several ways, but due to the construction of the reactor system the used measurement is performed with calibrated mercury thermometer.

is directly related to the pH-value of the substrate. Analysis of the concentration of volatile fatty acids is performed in accordance with the Method 5560 - Organic and volatile acids C [12]. Phosphorus content has been determined by the standard method BAS EN ISO 6878:2006 [13]. Phosphorus is the substrate of the organic, orthophosphate or polyphosphate form, therefore, the method is based on the translation of the entire content of phosphorus in the orthophosphates prior to the determination. To determine the chemical oxygen demand, the standard method is used according to the ISO 6060:2000 [14]. Preparation of samples for determining the concentration of heavy metals has been performed according to the standard method ISO 11464:1994 [15], and the monitoring of the concentrations has been performed of atomic absorption spectrometer (AAS) Perkin Elmer Precisely Analyst 200. Measuring the volume of biogas produced in the reactor has been performed in accordance with DIN 38 414, part 8 [16], and gas composition analysis has been performed on a gas chromatograph "PERKIN ELMER", equipped with the software package "Arnel".

The composition of the substrate during the production process changes due to the action of microorganisms, and it is possible to use a substrate that does not contain more than 15% dry matter. If, during the process, dry matter is reduced to 5%, the process is still running, but economically that is not further justified [22]. Hence, this parameter is important input characteristic of raw materials, while the minimum limit, at which the process can be stopped, is possible to be presented as the content of organic volatile substances. The content of organic substances is an obligate parameter, since it

represents the fraction of solid material that can be converted into biogas, or is required for the expression of the specific yield of biogas. Animal waste, sewage sludge and municipal waste, in most cases have 70-90% of organic matter in the content of dry matter. The difference between these two parameters gives inert (mineral) content, which is an inorganic content of the sample [23].

Since the pH of the substrate affects the growth of methanogenic microorganisms and flow process of anaerobic digestion, and bearing in mind that for the purposes of loosening phase anaerobic process requires a different range of pH values, this parameter is indispensable to control the process, especially if the process leads to controlling the pH in the reactor. Process is severely inhibited if the pH-value falls below 6 or rises above 8.3 [24, 25, 26]. Since it is directly related to the concentration of organic fatty acids and free ammonia pH is fast, reliable and inexpensive way to track the balance, especially in a system with low buffering capacity [6, 27]. Most organic substrates that undergo to anaerobic process are rich in nutrients and the problem is actually with excess of nutrients, especially of nitrogen as is in the further process leading to the formation of inhibiting ammonia [28]. Because the nitrogen in the substrate is generally in the organic form, the determination of total Kjeldahl nitrogen in the input substrate with possible measurement of total phosphorus and organic matter meets the required number of parameters, since it is possible to present the characteristics of the substrate through the ratio of C:N:P. Concerning this, knowledge of the value of the content of other forms of nitrogen or phosphorus is not mandatory to control the process. However, it should be noted that the equipment for determining the carbon content expressed as TOC requires quite large financial investment, but the method is quite slow and costly. Organic

matter content expressed through COD value represents a sufficient parameter, whose determination is much cheaper and faster than the parameter TOC.

Since many substances have inhibitory or toxic effect, if their content exceeds the limit value, it is necessary to know the concentration of these substances, especially in the input stream of raw material that undergoes anaerobic digestion process. However, if the structure of the input substrate is well known it is sufficient to limit the measurement of the content of substances that may be present in the input substrate or co-substrate. In this regard, in this paper, the limit is set as the content of heavy metals, particularly to those who have inhibitory concentration for anaerobic processes, such as: chromium, copper, nickel, lead and zinc [29]. Since the heavy metal concentrations were not even close to inhibitory concentration and analysis of heavy metals represents the most expensive and slowest analysis in the entire process, the need for determination of heavy metals in substrates prior to analysis has to be considered.

Measuring the volume of biogas produced in this study did not require additional costs or additional spending time, because reactor's system was equipped with eudiometric pipes through which it was possible to simply read the produced volume. If the volume measurement is combined with an analysis of the composition of biogas, it is possible to easily calculate the yield of methane, and therefore come to the conclusion if the process of anaerobic digestion is going in the right direction. An additional advantage of the determination of composition of biogas is knowledge about the share and the volume of oxygen in the gas mixture being produced, on the basis of which it is possible to conclude if the process is carried out under anaerobic conditions.

Other parameters listed above, which represent the characteristics of the substrates, is necessary to measure only if it is a specific type of substrate (e.g. the sugar content, if molasses is used as a raw material or waste

with a high sugar content), while in common substrates these parameters are directly related to elaborated ones (e.g. the content of suspended matter is directly related to the dry matter content).

CONCLUSION

If a set of parameters which can be analyzed at the beginning, during and/or at the end of the anaerobic process is divided into groups, so that all the parameters in a group are directly dependent from each other, it is possible to identify one or eventually two parameters as the representatives of the group whose values are necessary to know for reliable control of process. When identifying a representative group of parameters it is necessary to take into account the cost and duration of analysis, as well as the reliability of the obtained values.

It should be noted that based on the knowledge of the values of certain parameters, one can provide an optimal conditions for the process with corrective reaction during the process, where knowing

the values of other parameters represent only the information that the process is not in balance, without the possibility of changing the situation.

Based on the above mentioned, the minimum set of parameters necessary for the control of the anaerobic digestion includes primarily the measure of the temperature and pH-value of the substrate, the amount of organic matter in the reactor expressed by the amount of organic volatiles and/or COD, and definition of the optimal ratio of the feeding of nutrient substrate. In addition, knowing the yield and composition of the produced biogas can greatly facilitate the process control, and pre-empt the possible completion of the process, after which it is not economically justified to run it.

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